



GB042784



## PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

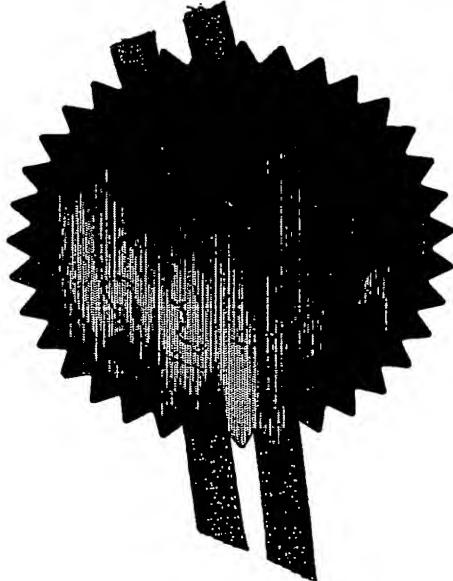
RECEIVED	
16 AUG 2004	
WIPO	PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Dated 2 August 2004



1  
26 JUN 03 EB17633-2 D02000  
P01/7700 0.04-0314824.4

The Patent Office

Cardiff Road  
Newport  
South Wales  
NP10 8QQ

## Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference

SGC/25037

2. Patent application number

(The Patent Office will fill in this part)

0314824.4

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Design Blue Limited  
OXO Tower Wharf  
Bargehouse Street  
London  
SE1 9PH

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

A/1 11/03  
Q3

U.K.

8098683002

4. Title of the invention

Energy Absorbing Material

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

MATHYS & SQUIRE  
100 Gray's Inn Road  
London WC1X 8AL  
United Kingdom

1081001 ✓

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See note (d))

YES

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

Continuation sheets of this form

Description 14

Claim(s) 5

Abstract -

Drawing(s) 5

10. If you are also filing any of the following, state how many against each item.

Priority documents -

Translations of priority documents -

Statement of inventorship and right to grant of a patent (Patents Form 7/77) 1

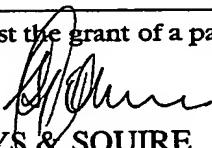
Request for preliminary examination and search (Patents Form 9/77) 1

Request for substantive examination (Patents Form 10/77) -

Any other documents (Please specify) -

11.

I/We request the grant of a patent on the basis of this application.

Signature 

Date

MATHYS & SQUIRE

25 June 2003

12. Name and daytime telephone number of person to contact in the United Kingdom

Stephen Colmer - 020 7830 0000

**Warning**

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

**Notes**

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

## ENERGY ABSORBING BLENDS

This invention relates to energy absorbing materials e.g. of the kind employed in systems designed for the protection of humans, animals or objects from damage by

5 impact; referred to hereinafter as impact protection systems.

Conventionally, impact protection systems have employed, as the energy absorbing material, elastomeric foams or similar relatively soft, resiliently compressible materials. However, only limited protection is achieved. In some systems, this

10 energy absorbing material is employed in combination with a rigid member the purpose of which is to spread the impact force over a greater area and therefore reduce its effect. However, such systems tend to be inflexible and uncomfortable if in contact with a human body. Most vulnerable areas of the body which require protection, e.g. elbows and knees, undergo significant changes in geometry and  
15 thus any attempt to match a rigid load-spreading shape will usually fail. One solution is to introduce articulation into the rigid element but this can compromise performance and increases cost.

More recently, proposals have been made for the use of strain-rate sensitive shear  
20 thickening silicone putty materials, sometimes known as silicone dilatants, in or as energy absorbing materials in impact absorption systems. By a strain-rate sensitive shear thickening material or dilatant, we mean a material which viscously flows at low rates of strain deformation but, at an elevated strain rate of deformation, undergoes a substantial increase in viscosity with rate of change of deformation. At

25 significantly higher deformation rates, such as those induced by a sudden impact, the material becomes substantially stiff or rigid. For example, US-A-5599290 describes a bone fracture prevention garment which employs, as the dilatant or shear-thickening material, a dispersion of solid particles in a viscous fluid. GB-A-2349798 describes an energy absorbing pad including a putty-like dilatant. However,  
30 in both cases, the dilatant has to be contained in an envelope because of its non self-supporting nature. The products therefore tend to have limited flexibility, are prone to damage by puncture, and require relatively complex and expensive

manufacturing processes. These products also tend to be heavy due to the relatively high density of the dilatant, which can be above 1000 kg/m<sup>3</sup>, and suffer from migration of the dilatant within the envelope as the dilatant will exhibit viscous flow at even very low levels of loading.

5

Other approaches for the utilisation of silicone dilatants have been to combine this material with a resilient carrier such as polyurethane foam.

In our copending International patent application PCT/GB02/05886 we have  
10 described and claimed a self supporting energy absorbing composite comprising:

- i) a solid foamed synthetic polymer matrix;
- ii) a polymer-based dilatant, different from i), distributed through the matrix and incorporated therein during manufacture of i); and
- iii) a fluid distributed through the matrix, the combination of matrix,  
15 dilatant and fluid being such that the composite is resiliently compressible;

and a self supporting energy absorbing composite comprising:

- i) a solid, closed cell foam matrix;
- ii) a polymer-based dilatant, different from i), distributed through the matrix; and
- iii) a fluid distributed through the matrix, the combination of matrix,  
20 dilatant and fluid being such that the composite is resiliently compressible.

Such compositions are not claimed in the present application.

25

The present invention provides an energy absorbing material suitable for use in or as an impact absorption material and which is self-supporting and relatively light weight; e.g. 100-500 kg/m<sup>3</sup>. The density can be tuned to specific applications. On occasion, a higher density material may be appropriate for certain applications.

30

According to the present invention, there is provided a composite material which is elastic, which exhibits a resistive load under deformation which increases with the

rate of deformation, which is unfoamed or foamed, comminuted or uncommunited and which comprises i) a first polymer-based elastic material and ii) a second polymer-based material, different from i), which exhibits dilatancy in the absence of i) wherein ii) is entrapped in a solid matrix of i), with the provisos that:

5

a) when the solid matrix of i) comprises a foamed synthetic polymer and a fluid distributed therethrough second material ii) is not distributed through the matrix and incorporated therein during the manufacture of i) such that the combination of matrix, dilatant and fluid results in a composite that is resiliently compressible; or

10

b) when the solid matrix of i) comprises a closed cell foam and a fluid distributed therethrough second material ii) is not distributed through the matrix such that the combination of matrix, dilatant and fluid results in a composite that is resiliently compressible.

15

It is preferred that the composite material is resistant to permanent set under all types of loading; e.g. compression, tension or shear or any combination thereof. By a solid matrix is meant herein a matrix material which retains its own boundaries 20 without need of a container.

Preferably, the first material i) and second material ii) are in intimate admixture; for example, as attainable by blending i) and ii) together. By blending is meant herein the mixing together of polymer based constituents i) and dilatant ii) in the semi- 25 molten or molten state to form a composite material wherein the first material i) and the second material ii) are in intimate admixture.

In addition to being self-supporting, the composite material of the invention offers a degree of impact protection which can exceed that of current rigid systems and 30 moreover, in the preferred embodiment wherein it is both flexible and resilient under all types of loading, it has the ability to conform to the geometry of what it is designed to protect by maintaining intimate contact through relatively large changes

in geometry. This is important for the design of protective components because induced damage is a function of the maximum force resulting from the impact divided by the area over which this force is distributed. The composite material of the invention enables both a reduction in the force and an increase in the area on 5 which the force acts or is reacted, thereby significantly reducing the resulting pressure or stress transmitted for a given impact event. It also offers the ability to exhibit some conformity to the impactor and thus produce additional force absorption as well as favourable geometry in terms of abrasion resistance. By means of the invention, it is also possible to achieve improved performance 10 compared to the use of an equivalent mass of dilatant when used on its own.

The first material i) may be one wherein the polymer comprising the first material i) comprises EVA or an olefin polymer, for example polypropylene or an ethylene polymer such as high pressure polyethylene (LDPE), LLDPE or HDPE.

15 Preferably, the polymer comprising the first material i) comprises an elastomer. While natural elastomers, e.g. latex rubbers, may also be used, our preference is for synthetic elastomers, more preferably synthetic thermoplastic elastomers such as thermoplastic polyesters. Preferred classes of such elastomers include 20 elastomeric polyurethanes and elastomeric EVAs (ethylene/vinyl acetate copolymers) ~~but it is expected that others such as silicone rubbers and EP rubbers,~~  
e.g. EPDM rubbers may also be suitable.

Other solid plastics materials may also be suitable for use as the polymer 25 constituent of the first material i) provided that they too exhibit an appropriate level of resilience. Any polymer-based material, different from i), which exhibits dilatancy and can be incorporated into the chosen elastic constituent(s) of first material i) may be used as second material ii). By a polymer-based material which exhibits dilatancy is meant a material in which the dilatancy is provided by polymer alone or 30 by a combination of polymer together with one or more other components, e.g. finely divided particulate material, viscous fluid, plasticiser, extender or mixtures thereof, and wherein the polymer is the principal component. In one preferred embodiment,

the polymer comprising the second material ii) is selected from silicone polymers exhibiting dilatant properties. The silicone - based polymer is preferably selected from borated siloxane polymers. For example, the dilatant may be selected from filled polyborondimethylsiloxanes (PBDMSs) or any number of polymers where 5 PBDMS is a constituent. The dilatancy may be enhanced by the inclusion of other components such as particulate fillers.

The dilatant may be combined with other components in addition to the components providing the dilatancy, e.g. fillers, plasticisers, colorants, lubricants and thinners.

10 The fillers may be particulate (including microspheres or microballoons) or fibrous or a mixture of particulate and fibrous. One class of particularly preferred dilatants based on PBDMS comprises the borated silicone-based materials that are marketed under the generic name of silicone bouncing putties and are produced by various manufacturers. These include those by Dow Corning under product catalogue no. 15 3179; by Wacker GmbH under product numbers M48 and M29 and by The Polish Chemical Institute under the product name Polastosil AMB-12. Other companies such as Rhodia, GE Plastics, ICI have also produced these materials, and other polymer-based dilatant materials having similar dilatancy characteristics, e.g. a similar modulus at low rates of strain and a similar plot of modulus against with 20 respect to the applied strain rate.

It is believed to be the presence of the borated cross-link within the composite material which enables it to exhibit a resistive load under deformation which increases with the rate of deformation. This type of cross-link is considered

25 temporary because it is believed to form reversibly and only or mainly during high rates of deformation of the polymer. In the PBDMS polymer this effect inhibits the siloxane chains from sliding during high rates of strain thus instantaneously inhibiting viscous flow. In this condition the polymer will therefore behave more like an elastomer. The composite material of the invention also possesses the borated 30 cross-links which enable it to exhibit the aforementioned behaviour. Other polymers that exhibit a temporary cross-link in the manner of PBDMS may also be used.

The composite material of this invention is preferably comminuted for ease of handling; for example, in transportation or for moulding purposes.

In accordance with another aspect of this invention, there is provided a process for

5 the preparation of a composite material according to the herein-described invention, which process comprises:

- a) melting the polymer intended to comprise the first material i); and
- b) blending the polymeric dilatant intended to comprise the second material ii) therewith.

10

Preferably, the polymeric dilatant is melted prior to and/or during the blending step (b). Suitably, after blending and cooling, the composite material so formed is c) comminuted.

15 One preferred method of forming the blend is first to form microspheres of second material ii) coated, for example with a polymer such as an elastomer, to prevent coalescence. These coated microspheres are then introduced into the first material i) which is either comminuted or in the melt.

20 This invention further provides a composite material prepared by a herein-described process of this invention.

---

In accordance with an important aspect of this invention, there is provided a composite material prepared by a herein-described process of this invention which

25 has subsequently been foamed; suitably, the so-produced foam is a closed cell foam. Suitably, at least part of the polymeric dilatant ii) is included within cell walls of the foam.

It is preferred that the cells include, as pneumatogen, a gas or vapour; for example, 30 nitrogen. Usually, the gas or vapour will be substantially uniformly dispersed throughout the matrix but non-uniform dispersion may be desirable in certain cases. The contribution of the gas or vapour to the resilient compressibility may be due to

redistribution of gas or vapour within the matrix or compression of the gas or vapour (or, indeed, both of these effects). The presence of the gas or vapour within the composite material not only significantly reduces the overall density of the composite but can also provide an amount of damping within the system due to pumping losses

5 associated with a pneumatic effect. The compressive resilient will also be enhanced by a pneumatic effect which will increase with the ratio of closed to open cells in the foam. An amount of pneumatic damping is desirable when considering energy absorption during impact and will further enhance the reactive nature of the composite.

10

An important property of the foam is the rate at which it recovers after being subjected to deformation, especially compression. Preferably, recovery is complete or substantially complete within a few seconds, e.g. 5 seconds or less, more preferably 2 seconds or less. In certain applications however a slower rate of 15 recovery may be desirable.

The foamed composite material of the invention may be prepared by combining the polymer intended to comprise the first material i); the polymeric dilatant intended to comprise the second material ii); and the gas or vapour or precursor thereof such 20 that the dilatant and the gas or vapour are distributed, generally substantially uniformly, throughout the matrix to produce a resiliently compressible material which exhibits a resistive load under deformation which increases with the rate of deformation. Whatever process is used, however, while the dilatant may be incorporated into the structure of the foam it is important that it does not completely 25 displace the gas or vapour from the pores.

One such process comprises incorporating an unfoamed composite material according to the herein-described invention into a hermetic container including means for supplying a pneumatogen thereinto; heating the composite material to an 30 elevated temperature at an elevated pressure; and injecting pneumatogen into the composite material. Suitably, the interior of the container is formed as a mould.

In a yet further method, the polymer intended to comprise the first material i) and the polymer-based dilatant intended to comprise the second material ii) are combined to form an intimate admixture, and the resultant mix is then foamed to form the composite. The methods employed can be selected from a number of recognised

5 industrial processes such as the various chemical or physical blowing methods. An additional preparatory process using a very high pressure nitrogen environment is also possible. This process uses a solid extruded section of the blend which is cross-linked (chemically or by irradiation) then subjected to a temperature and pressure cycle in an autoclave which is charged with nitrogen. The temperature will

10 soften the material to aid solubility of the gas, which is at very high pressure (10,000psi). This process may take several hours depending on the material and the thickness used. After this first autoclave process the resulting material has tiny bubbles of trapped nitrogen at very high pressure. A secondary lower pressure/temperature cycle then allows the trapped nitrogen to expand the

15 surrounding material to form a foam. The exact pressure and temperature cycle of this second process will determine the final density of the foam produced. This process is used by Zotefoams, Croydon, UK.

In a still further process according to the invention the foamed composite material

20 of the invention may be prepared using, as pneumatogen, microspheres comprising a polymeric shell which hermetically encapsulates a gas (EXPANCEL by Akzo

---

Nobel, for example). The microspheres may be mixed with the first material i) or coated with the second material ii) (or, indeed, both) before blending i) and ii). On heating the produced blend, the gas in the microspheres expands (the expansion

25 may be ca 40x) to create closed cells.

The composite material of the invention may include components other than the polymer intended to comprise the first material i), the polymer-based dilatant intended to comprise the second material ii) and the gas or vapour; e.g., fibrous

30 and/or particulate fillers, plasticisers, lubricants, extenders, pigments and dyes. If desired, the composite of the invention may be incorporated within an envelope which may be rigid or flexible, but it is valuable feature of the invention that such

containment is not essential.

Likewise, it may be associated with a rigid or semi rigid component but this is not essential for the use of the composite and may even compromise some of its  
5 properties for certain applications.

Furthermore, it may also be associated with a textile layer or similar where the textile  
has the facility to enhance the abrasion performance and in some cases the  
resistance to intrusion from sharp objects and/or assist in the attachment of the  
10 composite material to other systems or products.

In accordance with a further aspect of this invention, the final properties of the composite material as hereindescribed, such as resilience, strain rate sensitivity, tensile strength, hardness, elastic modulus, and creep modulus, may be carefully  
15 controlled by the use of compatibilisers or crosslinking (or indeed both). Crosslinking may be chemical crosslinking or physical crosslinking (such as by irradiating or by entanglement polymerisation) and may be undertaken on first material i) or the second material ii) (or, indeed, both). The first material i) may be crosslinked to the second material ii).

20

In general, the composite material of the invention will exhibit resistance to creep and compression set. A low creep modulus of the composite modulus will be beneficial, but not essential, to imparting resistance to compression set. In some applications it may be preferred to allow the material to have high creep  
25 characteristics; for example, for second insulation purposes.

The actual constitution of the composite material of the invention will be influenced by the intended application. Applications cover a wide range of uses and include impact protection for objects, animals and humans. Potential applications extend  
30 to any dynamic situation where the object may already be in contact with a surface and the combination of object and surface may undergo severe acceleration and/or deceleration, e.g. as in packaging for delicate equipment or a human body in a

vehicle seat. Thus, the nature of the composite material and the choice and blending ratio of the dilatant in the composite material and, where foamed, the amount of gas or vapour in the composite material, e.g. as indicated by the required density of the composite material, will be determined by the requirements of the protective system in which the composite material is to be employed. In general, the dilatant will form from 5 to 80%, preferably 10 to 50%, more preferably 15 to 40% by volume of the composite, and where foamed, the amount of gas or vapour (in the preferred case where it is a gas) will be such that the gas or vapour content of the composite is preferably from 20 to 90%, more preferably from 30 to 80%, still more preferably from 40 to 70% by volume. It should be noted that these proportions are excluding the use of any fillers or other additional components.

Still further according to the invention there are provided shaped articles, e.g. extruded articles such as films, sheets, filaments and fibres, comprising the composite materials of the invention. Shaped articles such as textured sheets of the composite may have the texture geometrically configured such that compressive deformation will advantageously deform the elements comprising the texture to optimise the reactive nature of the composite. This is particularly beneficial in closed cell foam. The shaped article may, if desired, be produced in such a way as to include regions or layers in which the ratio of dilatant within the composite material differs from that in other regions or layers. In this way the distortion of the shaped article, e.g. fibre or filament, may be configured to facilitate maximum shear deformation shearing of the dilatant rich regions at the dilatant/matrix interface.

The fibres or filaments may be woven, knitted or otherwise configured such as to incorporate air into the final product. When such a material is subjected to impact, the distortion of each fibre is facilitated by the air spaces to provide a large number of localised bending deflections, which is preferable for the efficient use of the composite material in absorbing impact.

30

The choice and concentration of the first material i) is preferably such as to allow the shaping of the composite material e.g. into fibres or filaments. In low strain rate

movements, the flexibility of a textile comprising fibres or filaments formed from the admixture composite blend may be provided by choice of fibre weave or knit. Other fibres or filaments may be included in the textile, if desired, e.g., elastic fibres and/or abrasion-resistant fibres.

5

The fibre which may be formed, for example, by extrusion or spinning may have an even distribution of second material ii) within first material i) or may be manufactured to create regions or layers where the second material ii) is more concentrated.

10 In accordance with a still further aspect of this invention, there is provided a fibre which comprises a core of second material ii) within a sheath of first material i), wherein the first material i) and second material ii) are as hereindefined. The core may be hollow, preferably coaxially hollow. Such fibres may be made by coextrusion. Such a fibre is depicted in Fig. 1 of the accompanying drawings in

15 which 1 is a core of second material ii), 2 is a sheath of first material i) and 3 is a hollow containing a gas (air).

The energy absorbing composite material of the invention may be employed in a wide variety of applications; for example in protective pads or clothing for humans and animals, in or as energy absorbing zones in vehicles and other objects with which humans or animals may come into violent contact, and in or as packaging for delicate objects or machinery. Specific examples of applications are in headwear and helmets; protective clothing or padding for elbows, knees, hips and shins; general body protection, for example for use in environments where flying or falling objects are a hazard; vehicle dashboards, upholstery and seating. Other potential uses are in garments or padding to protect parts of the body used to strike an object e.g. in a sport or pastime; for example in footwear, such as running shoe soles, football boots, boxing gloves and gloves used in the playing of fives. The energy absorbing composite material of the invention may also be employed in non-impact situations; for example, in energy absorbing and damping materials such as automotive mounts and vibration isolation. This list is not intended to be exclusive and other potential uses will occur to the reader.

Examples are depicted in Figures 2 and 4 inclusive of the accompanying drawings.

Figure 5 of the accompanying drawings illustrates an example of use in footwear.

- 5 In order to provide favourable pressure characteristics and a greater level of support under shock loads transmitted through the sole of the foot during any type of active recreation, the composite material is utilised in the construction in the soles of footwear, e.g. innersoles, midsoles or outer soles. The example illustrates the use of the material between the innersole (1) and the outersole (2), where the interfaces
- 10 between both the innersole and midsole (3) and the outersole and midsole are favourably contoured or textured to induce large amounts of shear deformation in the foamed composite material of the invention. This type of construction may be formed by injecting a pre-mixed reaction based form of the foamed composite material into the cavity between the inner and outer sole such that the resulting
- 15 midsole solidifies and bonds to both the inner and outer sole. A similar structure is achieved as a one-part moulding whereby the reactive material foams within a mould, the inner and outer soles being formed by the "skin" produced at the mould surfaces.

20 A coating may be applied to the composite, if desired.

---

The following Examples illustrate the invention.

#### EXAMPLE 1

- 25 The elastic polymeric constituent material selected for a precursor blend process evaluation was a linear low density polyethylene (Flexirene MR50 by Europa Polymeri). Three dilatant materials were selected for blending trials in different ratios. The three dilatant materials were the Dow Corning silicone dilatant 3179,
- 30 Polastosil AMB-12 and pure PBDMS. These were blended with the LLDPE MR50 using a Shaws K1 3 litre intermix. The LLDPE was introduced into the mill in granular form first where the temperature generated through shearing the material

rose to around 110 deg C. The dilatant materials were then fluxed into the internal mixer in the ratios as specified below:

1. 35% 3179 65% LLDPE by weight.
- 5 2. 50% 3179 50% LLDPE by weight.
3. 50% Polastosil ABM-12 50% LLDPE by weight.
4. 35% Polastosil ABM-12 65% LLDPE by weight.
5. 30% PBDMS 70% LLDPE by weight.
6. 35% PBDMS 65% LLDPE by weight.

10

The above material blends were then dump extruded through 4 x 2mm diameter dies to form strands which were then pelletised.

## EXAMPLE 2

15

The purpose of this example is to show the potential for the invention to be manufactured to produce a closed cell structure, utilising existing manufacturing processes. One suitable manufacturing process that is currently employed for closed cell foam manufacture is the high-pressure nitrogen gas solution process. This 20 process takes a block of solid polymer material, and subsequently foams this block under high pressure and temperature using nitrogen. The advantage of the process for foam manufacture is the uniformity of the cellular structure and the lack of chemical deposition from conventional blowing agents.

25 In order to consider the invention for such a manufacturing process it is necessary to confirm that the mixture will be stable at the elevated temperatures of the manufacturing process. This is necessary in order to consider replacing the polymer sheet or block in the standard process with a prepared sample containing both the dilatant and the matrix material, as an intimate mix. The normal operating 30 temperature of the process is around 165°C.

The matrix material chosen for this example was Hytrel, which is a polyester based

thermoplastic elastomer available from Du Pont. The material comes in a number of grades, based upon the hardness that is desired, and for this experiment a 55-grade material was used. 50 grams of Hytrel and an equal weight of 3179 dilatant compound were placed in a crucible in preparation for mixing at high temperature.

- 5 A laboratory oven was preheated to 220°C and the crucible and contents placed in the oven and left for 30 minutes. The crucible was then removed and the contents stirred with a metal spatula to mix the two materials. The resulting mixture was then replaced in the oven and heat soaked for a further hour at this temperature, before removing for investigation. The two materials mixed very well to produce a
- 10 homogenous material that was solid at room temperature. The material was heated to 165°C in a laboratory oven and was found to be stable over a period of 8 hours, which is the duration fo the high-pressure nitrogen gas solution process. The results indicate the potential suitability of the sample for foaming: for example, using a high pressure nitrogen process or other physical or chemical blowing processes.

15

Without wishing to be bound by theory, it is believed (though not ascertained) that because the second material ii) (which exhibits dilatancy in the absence of the first material i) is entrapped in the composite material of the invention in a solid matrix of i) its ability to flow is inhibited such that, at high local deformation rate, its

- 20 tendency to shear thicken is efficiently imparted to the composite material which thereby exhibits a resistive load under deformation which increases with the rate of deformation.

---

- Furthermore, where the composite material is foamed the gas or air within the cell
- 25 will, by reason of its compressibility, allow the composite material to undergo larger amounts of local elastic deformation thereby extending the opportunity of the composite material to stiffen during impact. In the cases where the cells are closed cells, it is believed that additional pneumatic stretching of the cell walls gives rise to greater local elastic deformation.

**CLAIMS**

- 1) A composite material which is elastic, which exhibits a resistive load under deformation which increases with the rate of deformation, which is unfoamed or 5 foamed, comminuted or uncommunited and which comprises i) a first polymer-based elastic material and ii) a second polymer-based material, different from i), which exhibits dilatancy in the absence of i) wherein ii) is entrapped in a solid matrix of i), with the provisos that:
  - a) when the solid matrix of i) comprises a foamed synthetic polymer and 10 a fluid distributed therethrough second material ii) is not distributed through the matrix and incorporated therein during the manufacture of i) such that the combination of matrix, dilatant and fluid results in a composite that is resiliently compressible; or
  - b) when the solid matrix of i) comprises a closed cell foam and a fluid 15 distributed therethrough second material ii) is not distributed through the matrix such that the combination of matrix, dilatant and fluid results in a composite that is resiliently compressible.
2. A composite material according to Claim 1 wherein first material i) and 20 second material ii) are in intimate admixture; for example, as attainable by blending i) and ii) together.
3. A composite material according to Claim 1 or 2 wherein the polymer comprising the first material i) comprises EVA or an olefin polymer, for example 25 polypropylene or an ethylene polymer such as high pressure polyethylene (LDPE), LLDPE or HDPE.
4. A composite material according to Claim 1 or 2 wherein the polymer comprising the first material i) comprises an elastomer. 30
5. A composite material according to Claim 4 wherein the elastomer is a natural elastomer, such as latex rubber.

6. A composite material according to Claim 4 wherein the elastomer is a synthetic elastomer.
7. A composite material according to Claim 6 wherein the synthetic elastomer
- 5 is a silicone rubber, a polyurethane or an EP rubber such as EPDM.
8. A composite material according to Claim 6 wherein the synthetic elastomer is a thermoplastic elastomer.
- 10 9. A composite material according to Claim 8 wherein the thermoplastic elastomer comprises a polyester.
10. A composite material according to any one of the preceding claims wherein the polymer comprising the second material ii) is selected from silicone polymers
- 15 exhibiting dilatant properties.
11. A composite material according to Claim 10 wherein the silicone polymer is selected from borated siloxane polymers.
- 20 12. A composite material according to Claim 11 wherein the silicone polymer is selected from filled polyborodimethylsiloxanes.

---

13. A composite material according to any one of the preceding claims which is comminuted.
- 25 14. A process for the preparation of a composite material according to Claim 1, which process comprises:
  - a) melting the polymer intended to comprise the first material i); and
  - b) blending the polymeric dilatant intended to comprise the second
- 30 material ii) therewith.
15. A process according to Claim 14 wherein the polymer intended to comprise

the first material i) is defined in any one of Claims 3 to 9 and/or the polymeric dilatant intended to comprise the second material ii) is defined in any one of Claims 10 to 12.

5 16. A process according to Claim 14 or 15 wherein the polymeric dilatant is melted prior to and/or during the blending step (b).

17. A process according to Claim 14, 15 or 16 wherein, after blending and cooling, the composite material so formed is c) comminuted.

10 18. A composite material prepared by the process of any one of Claims 14 to 17.

19. A composite material according to any one of Claims 1 to 13 and 18 which has subsequently been foamed.

15 20. A composite material according to Claim 19 wherein the foam is a closed cell foam.

21. A composite material according to Claim 19 or 20 wherein at least part of the 20 polymeric dilatant ii) is included within cell walls of the foam.

22. A composite material according to Claim 19, 20 or 21 wherein the cells include, as pneumatogen, a gas.

25 23. A composite material according to Claim 22 wherein the gas comprises nitrogen.

24. A process for the preparation of a composite material according to Claim 19, which process comprises:

30 d) incorporating a composite material as defined in any one of Claims 1 to 13 or 18 into a hermetic container including means for supplying a pneumatogen thereinto;

- e) heating the composite material to an elevated temperature at a elevated pressure; and
- f) injecting pneumatogen into the composite material.

5 25. A process according to Claim 24 wherein the interior of the container is formed as a mould.

26. A foamed composite material prepared by the process of Claim 24 or 25.

10 27. A shaped article comprising a composite material according to any one of Claims 1 to 13, 18, 19 to 23 and 26.

28. A shaped article as claimed in Claim 27 in the form of a sheet, film, filament or fibre.

15 29. A fibre which comprises a core of second material ii) within a sheath of first material i).

30. A fibre according to Claim 29 wherein the core is hollow.

20 ~~31. A fibre according to Claim 29 or 30 wherein the first material i) is defined in any one of Claims 3 to 9 and/or the second material ii) is defined in any one of Claims 10 to 12.~~

25 32. A textile or web including filaments or fibres as claimed in any one of Claims 28 to 31.

33. An impact protection system including a composite material as claimed in any one of Claims 1 to 13, 18, 19 to 23 and 26; a shaped article as claimed in any one 30 of Claims 27 to 31 or a textile or web as claimed in Claim 32.

34. An impact protection system according to Claim 33 associated with a rigid or

semi-rigid component.

35. An impact protection system according to Claim 33 or 34 associated with a textile layer.

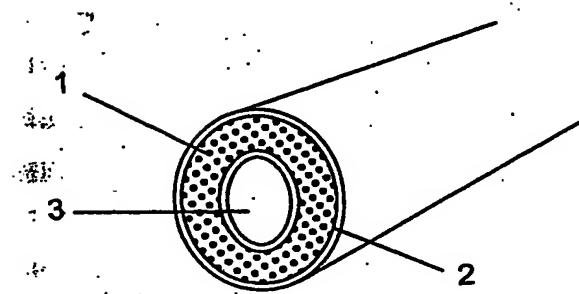
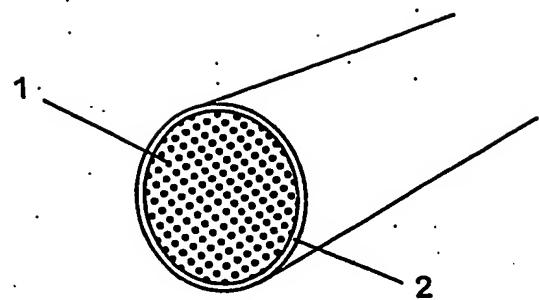


Fig. 2

hand component

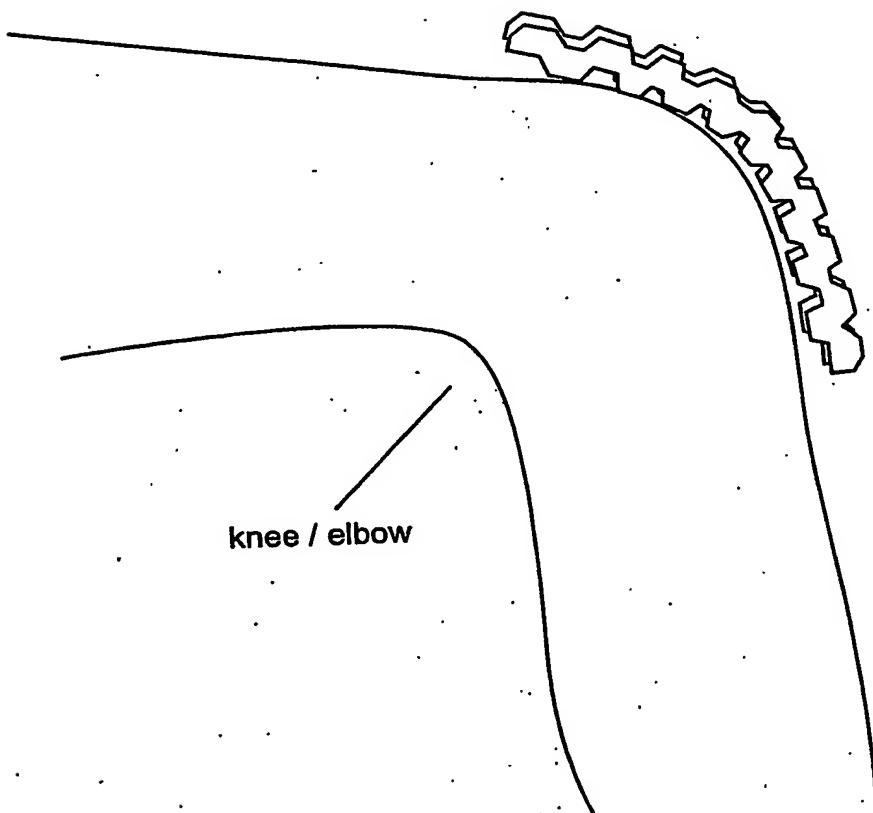
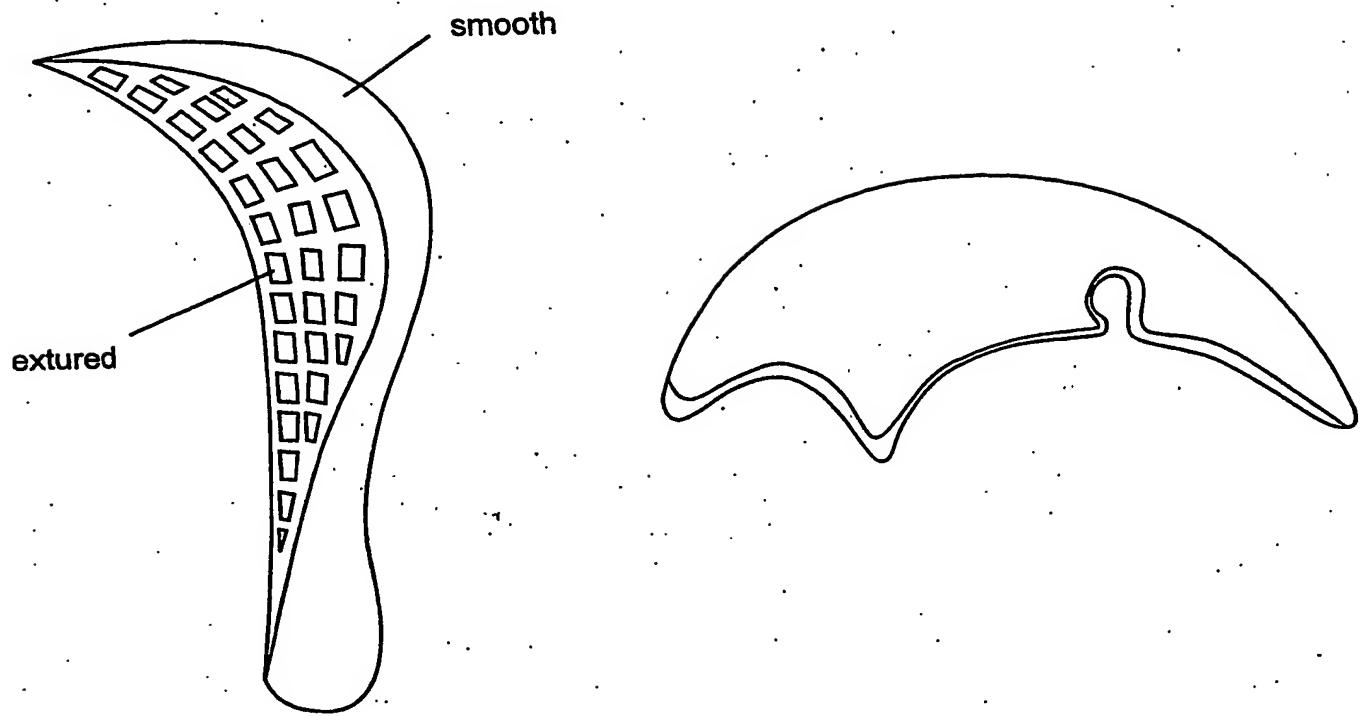
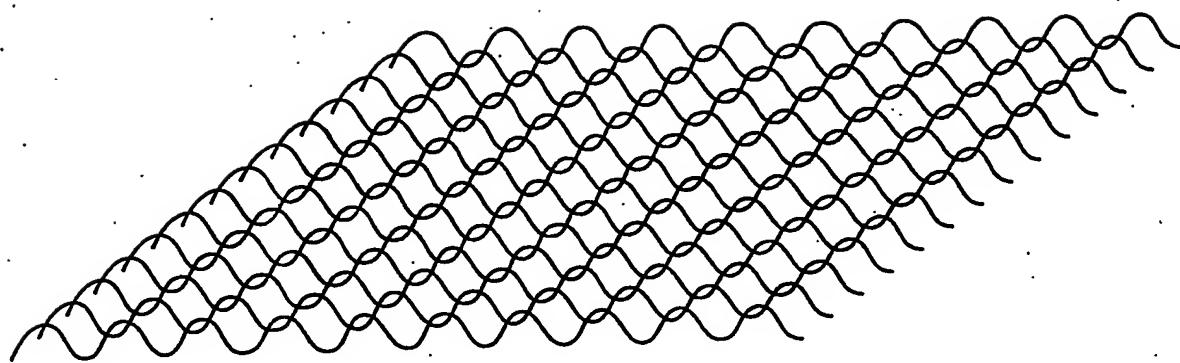
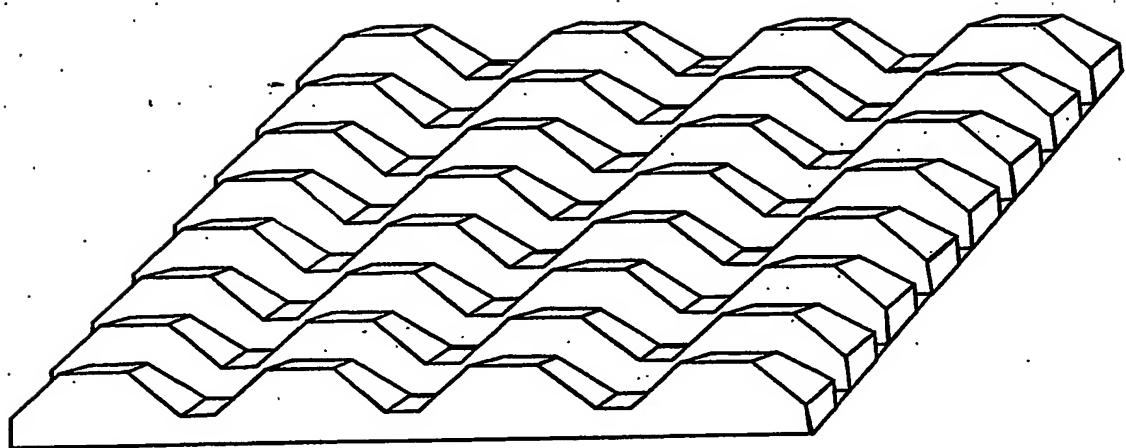


Fig. 3



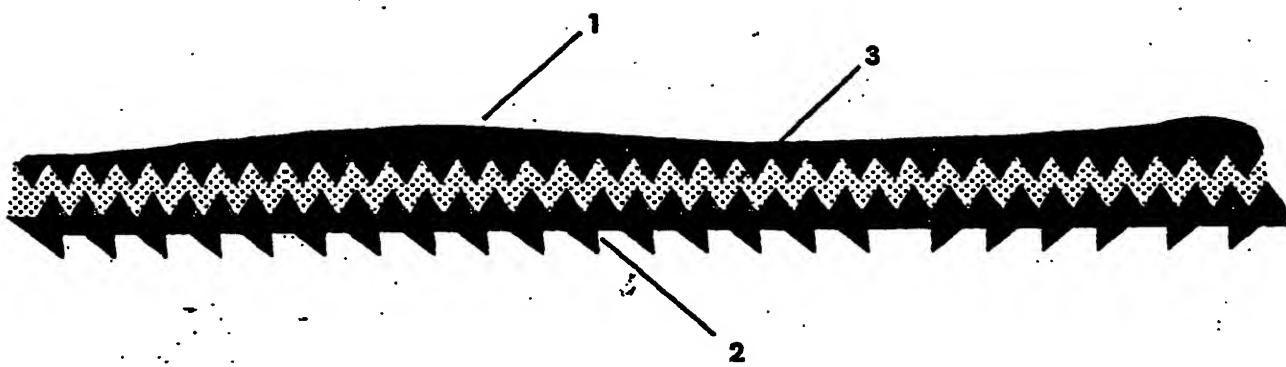
3D weave of hollow / solid fibres

Fig.



shaped sheet with permeability

Fig. 5



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER: \_\_\_\_\_**

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**